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Sustainable polymers: plastics from plants

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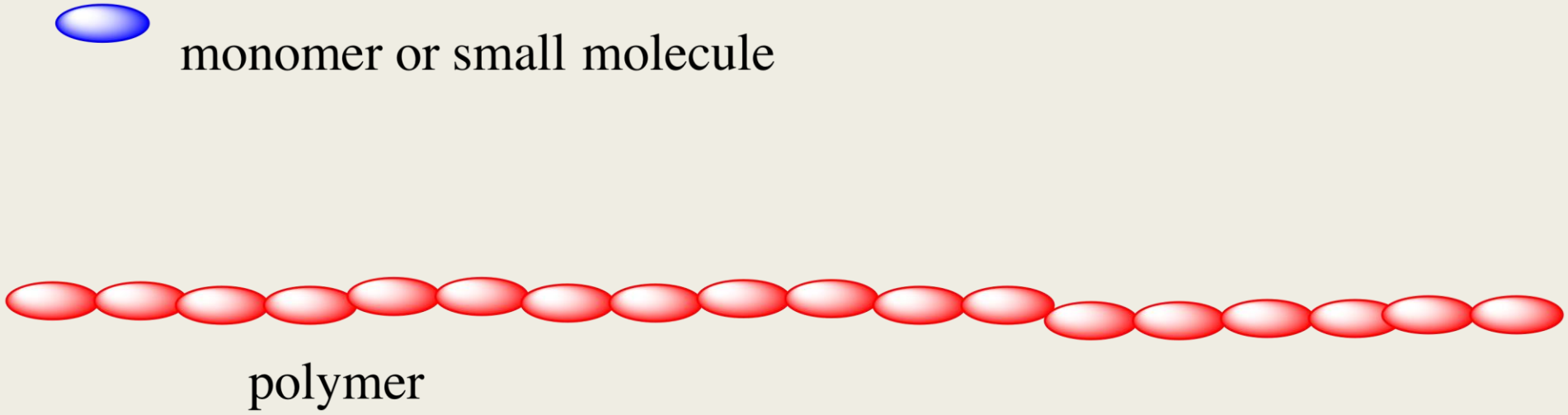
SUSTAINABLE POLYMERS

Chris P Schaller
CSB|SJU Chemistry Thursday forum: April 6, 2017

What are polymers?

- Very large molecules made from repeating units (monomers)

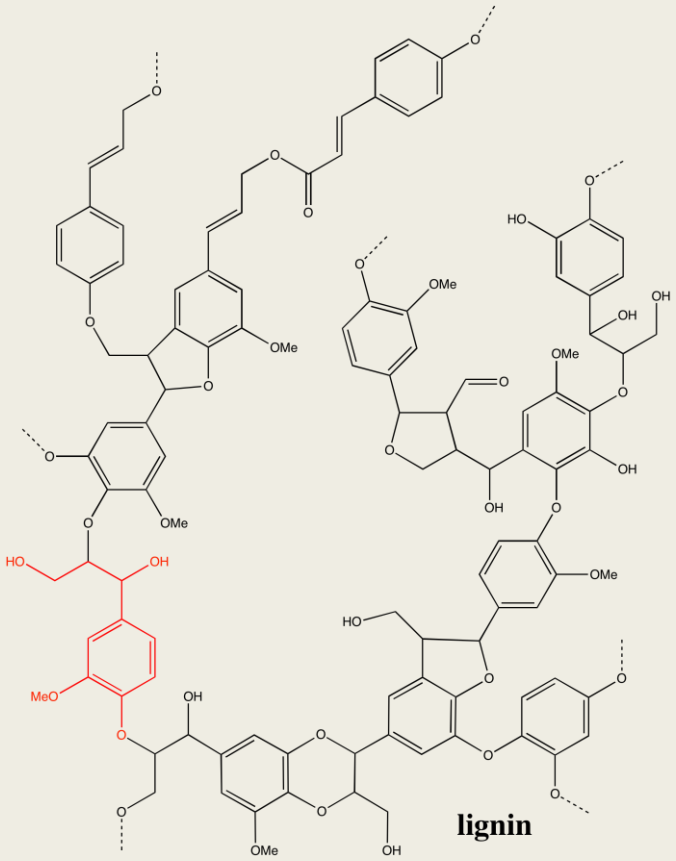


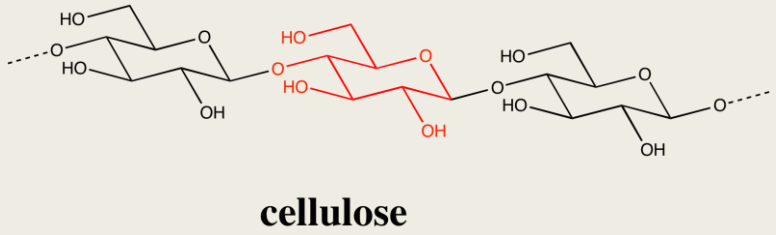
Making a polymer from monomers

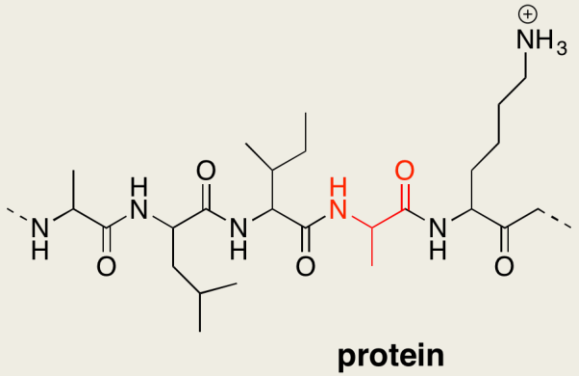
- 3D printing
- https://www.youtube.com/watch?v=mMkhVt_IWs4
- https://www.youtube.com/watch?v=UpH1zhUQY0c#t=60.395104

Biopolymers

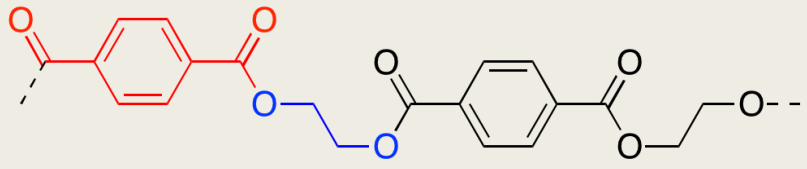
- Lignin (woody plants); cellulose (plants); proteins & DNA



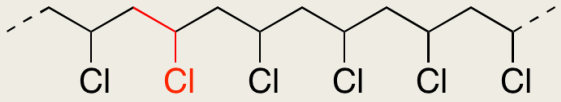




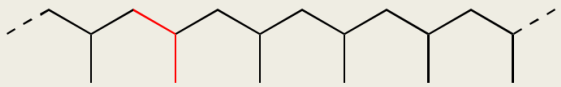
Commercial polymers



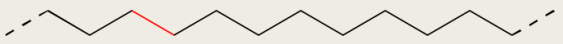
1 PETE



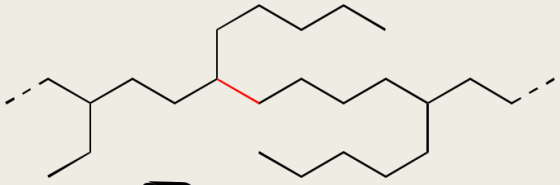
3 PVC



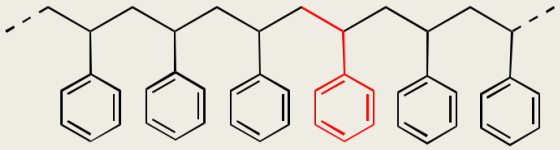
5 PP



2 HDPE

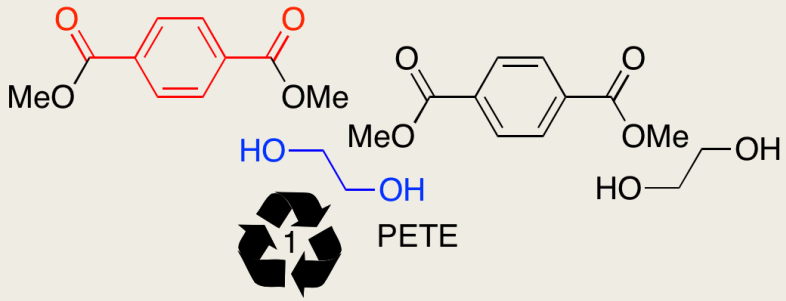


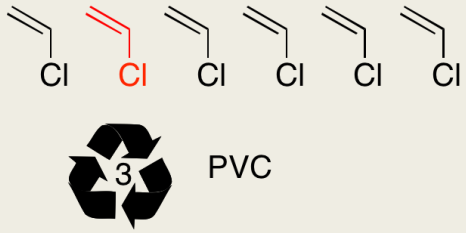
4 LDPE

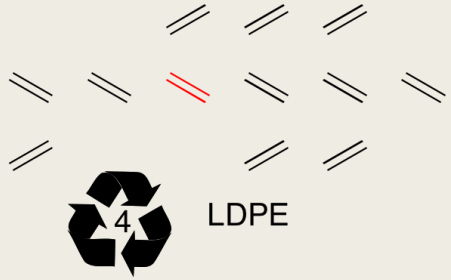


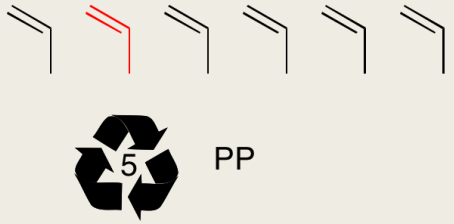
6 PS

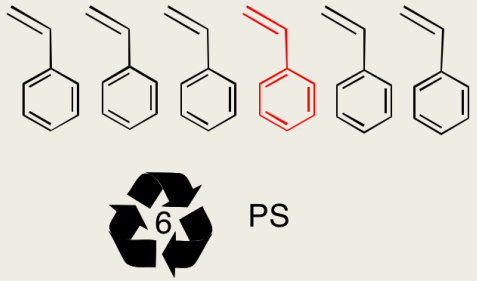
… and where they come from





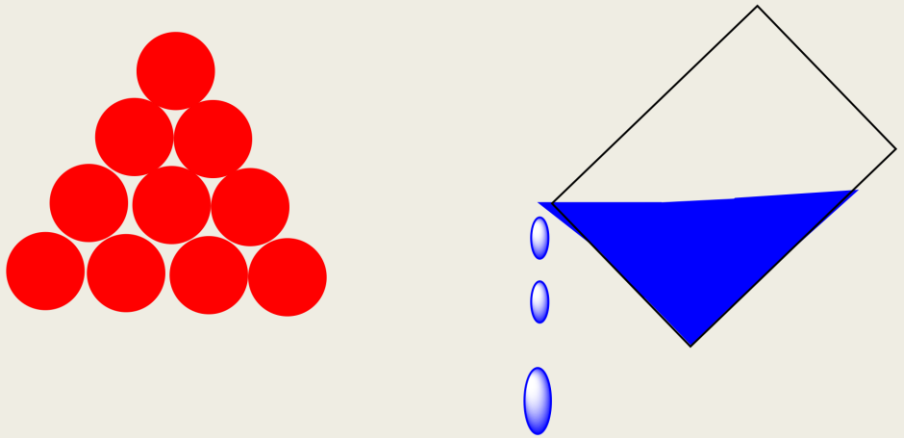






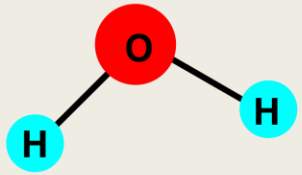
What makes polymers unique?

- Viscoelastic materials
- Behavioural elements typical of both solids and liquids

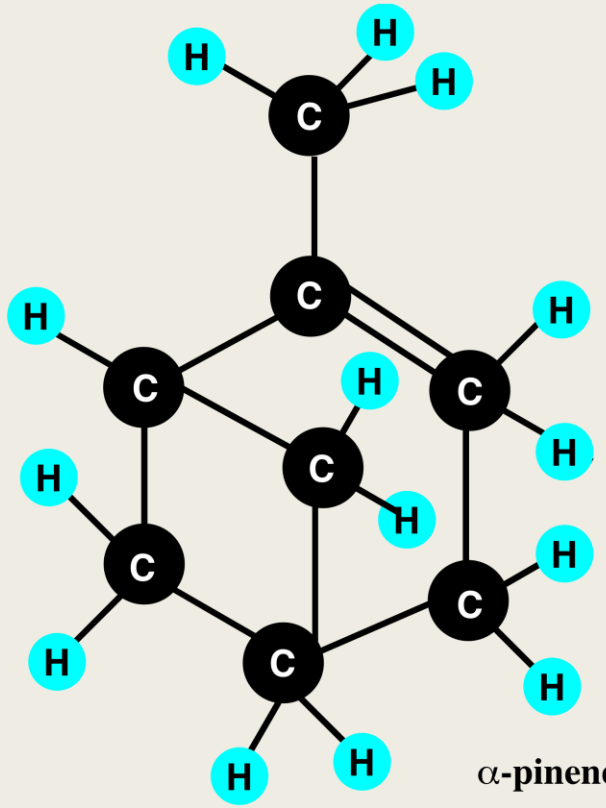


Liquids

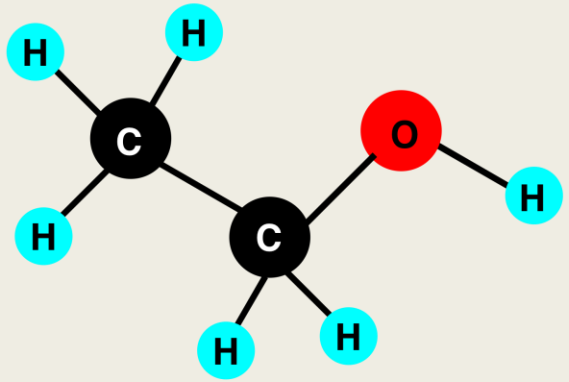
- Often made of *individual* molecules (water, turpentine, ethanol).



water



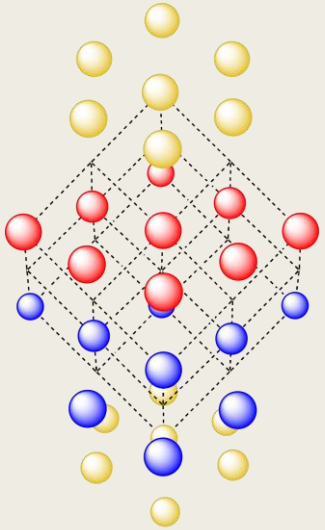
α-pinene



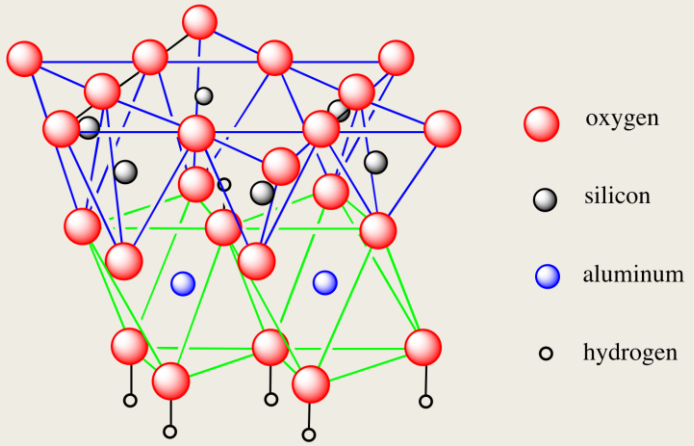
ethanol

Solids

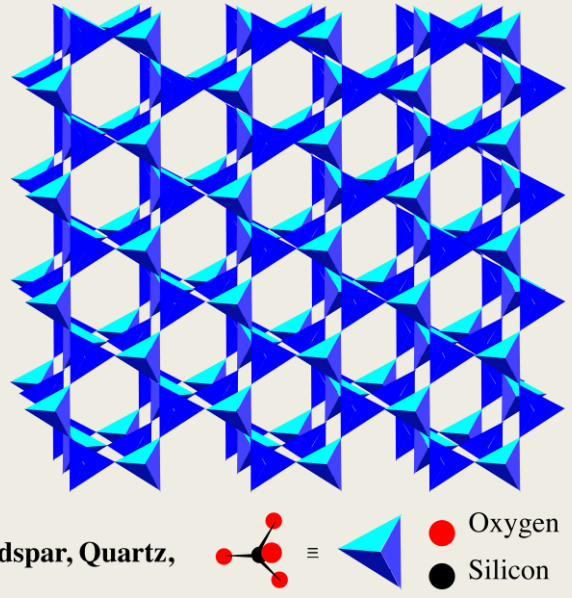
- Often made of *extended* structures of bonded atoms (metals, bricks, rocks).



Gold

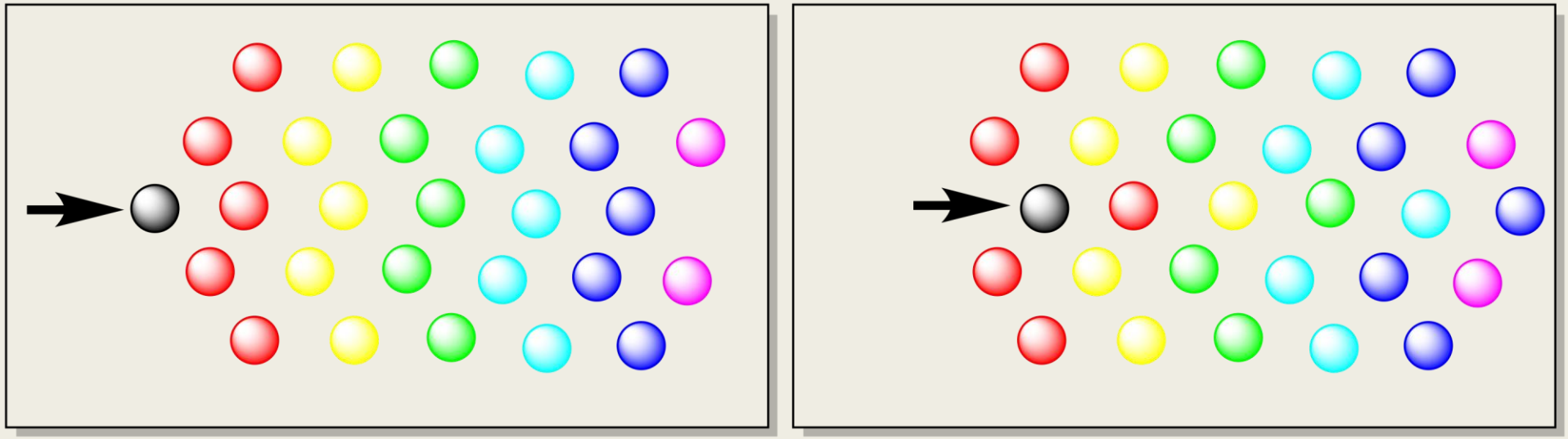


kaolin



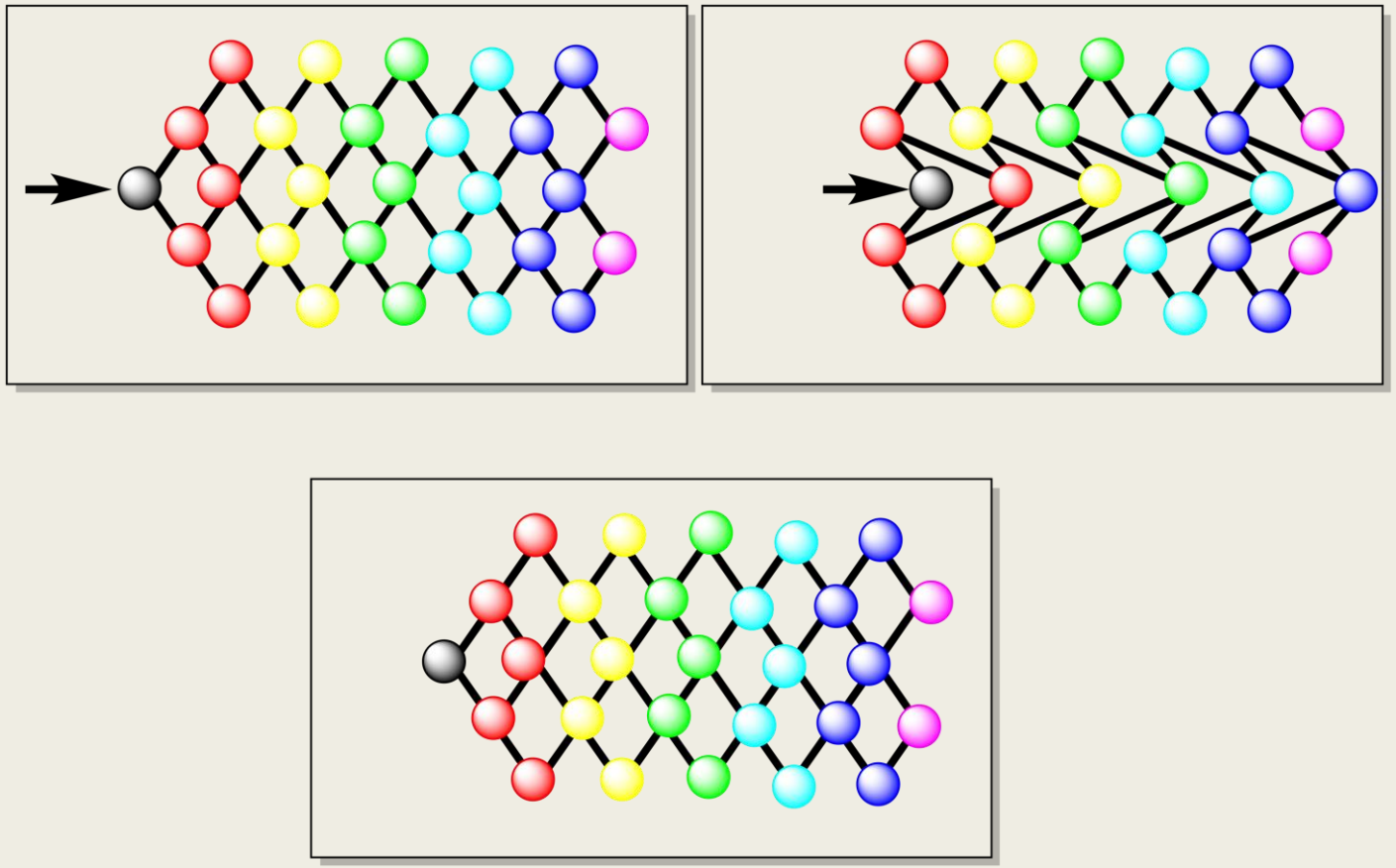
Viscous response to stress (liquids)

- Flow in response to applied force.



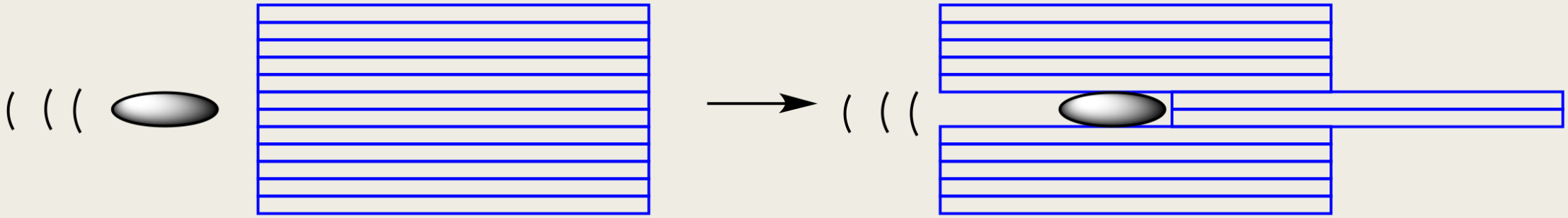
Elastic response to stress (solids)

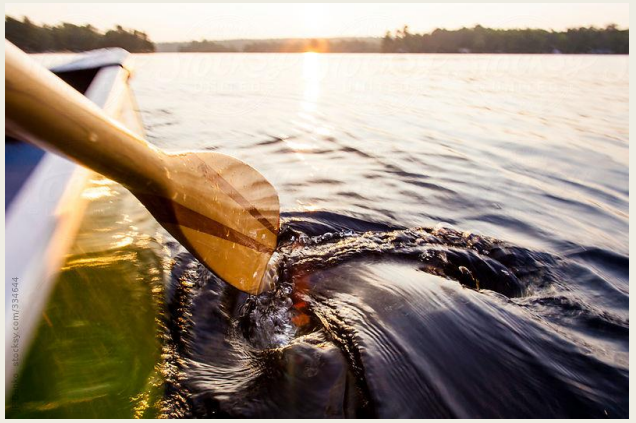
- Material retains its shape.



Low-viscosity fluid

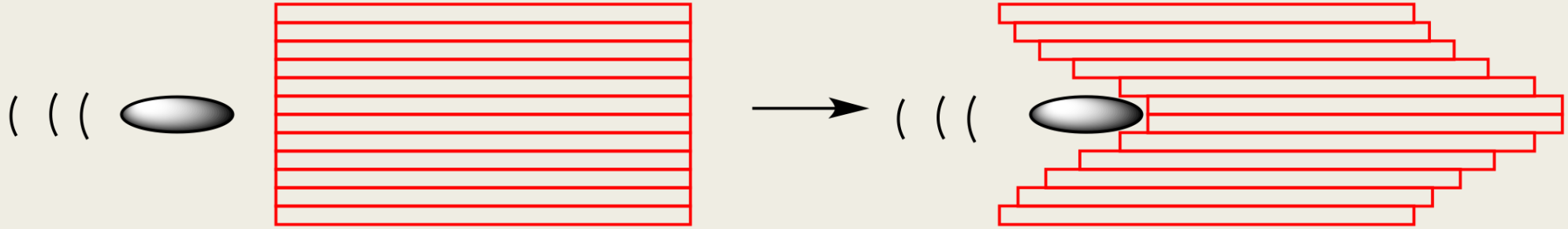
- Surrounding layers unaffected by flow



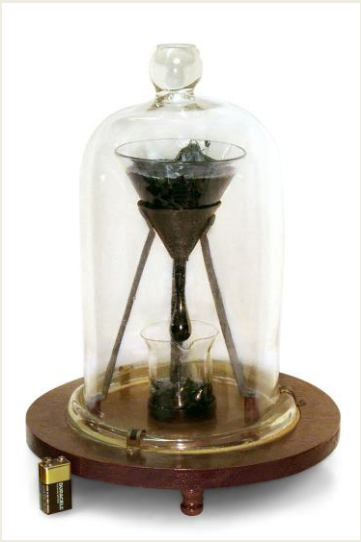


High-viscosity fluid

- Flow drags surrounding layers along

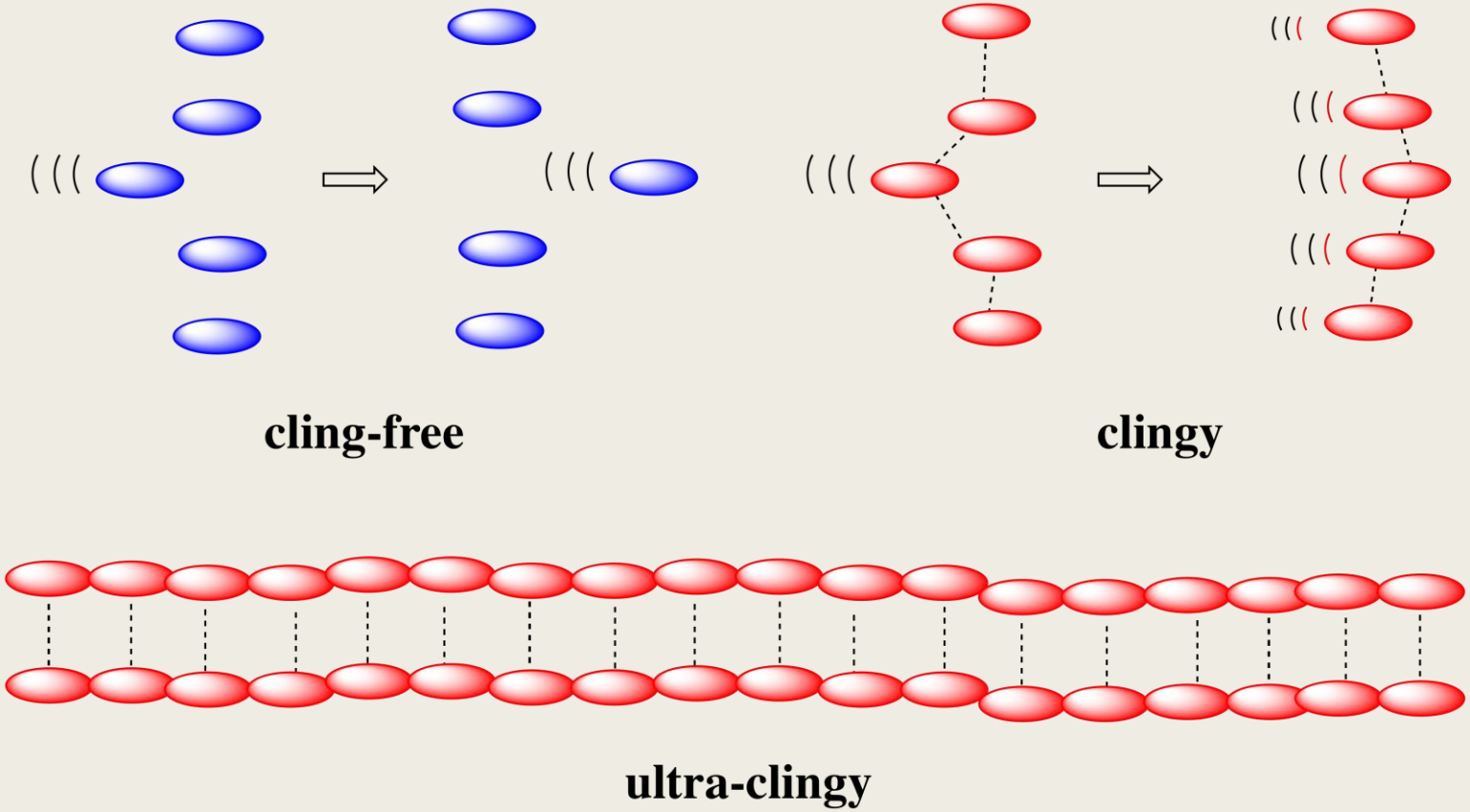


- http://www.thetenthwatch.com/



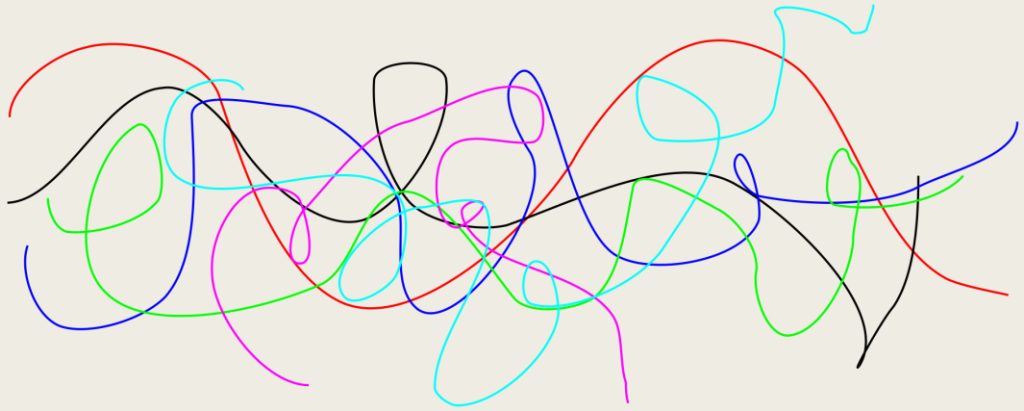
What causes drag?

- Clinginess



Entanglement

- Resistance to flow because of tangled chains (very high chain lengths)

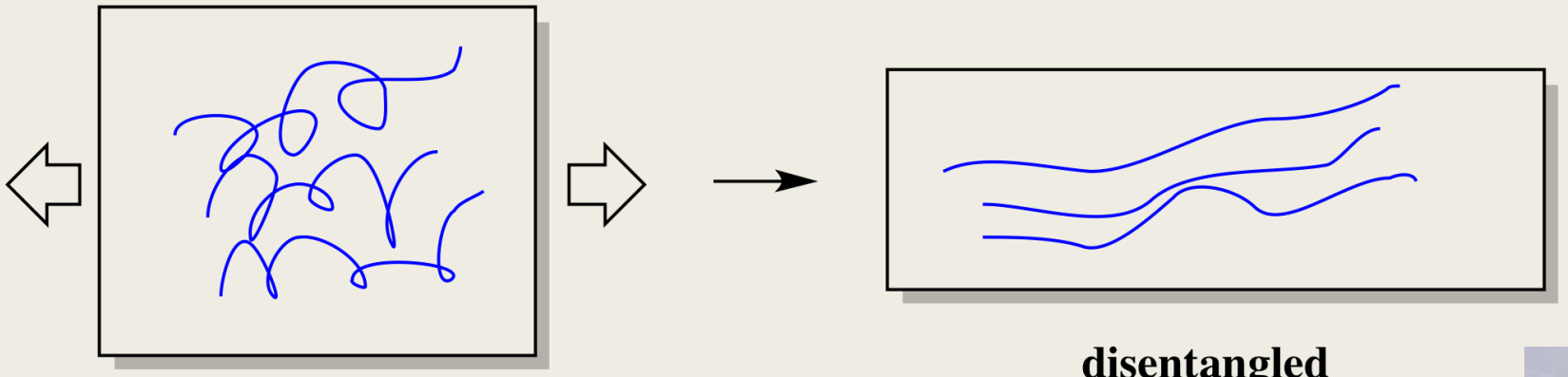


Viscoelastic response

- Elements of elastic (solid) and viscous (fluid) behaviour

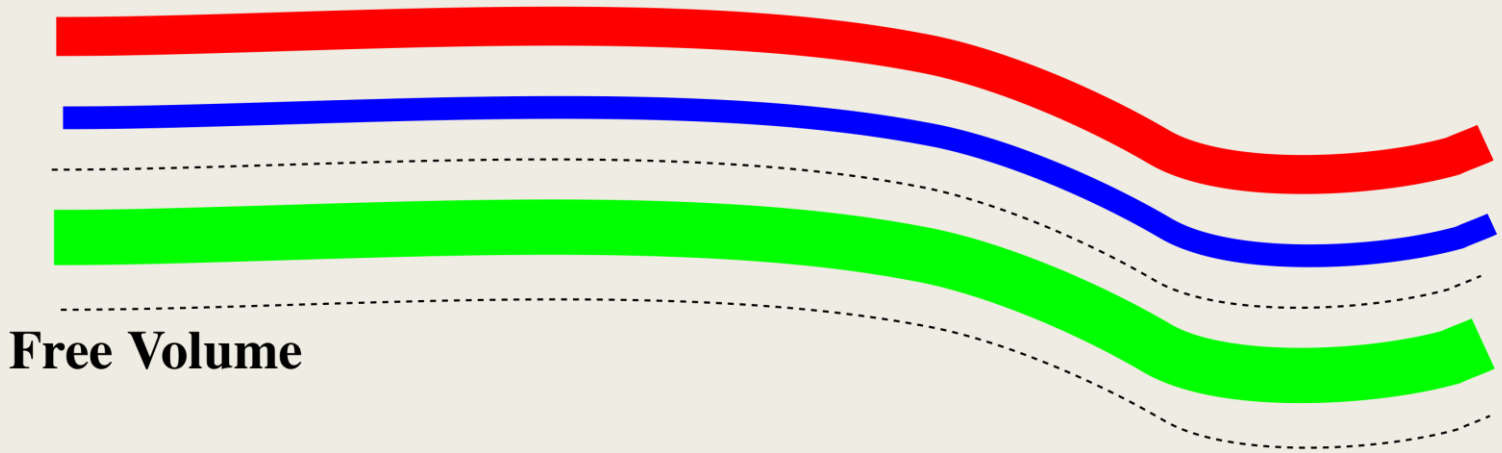
Unusual properties

- Shear thinning



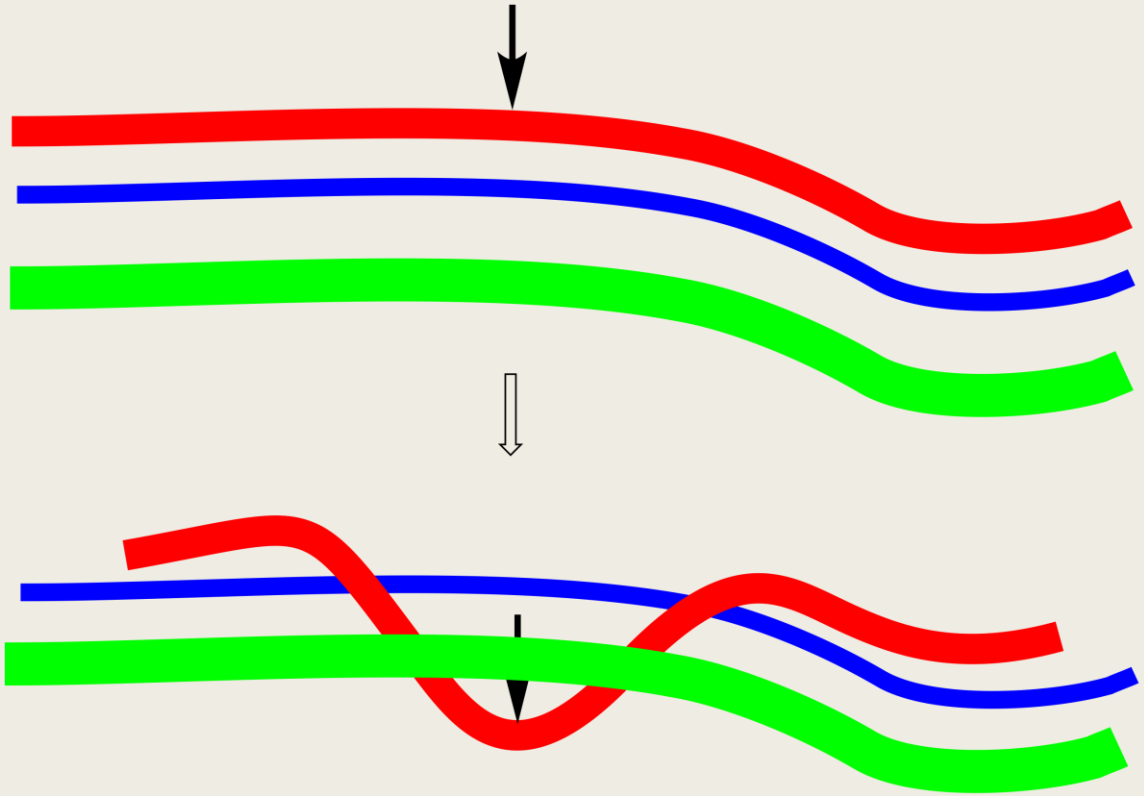
The glass transition temperature

- Temperature at which thermal expansion allows free volume sufficient for chain flow.



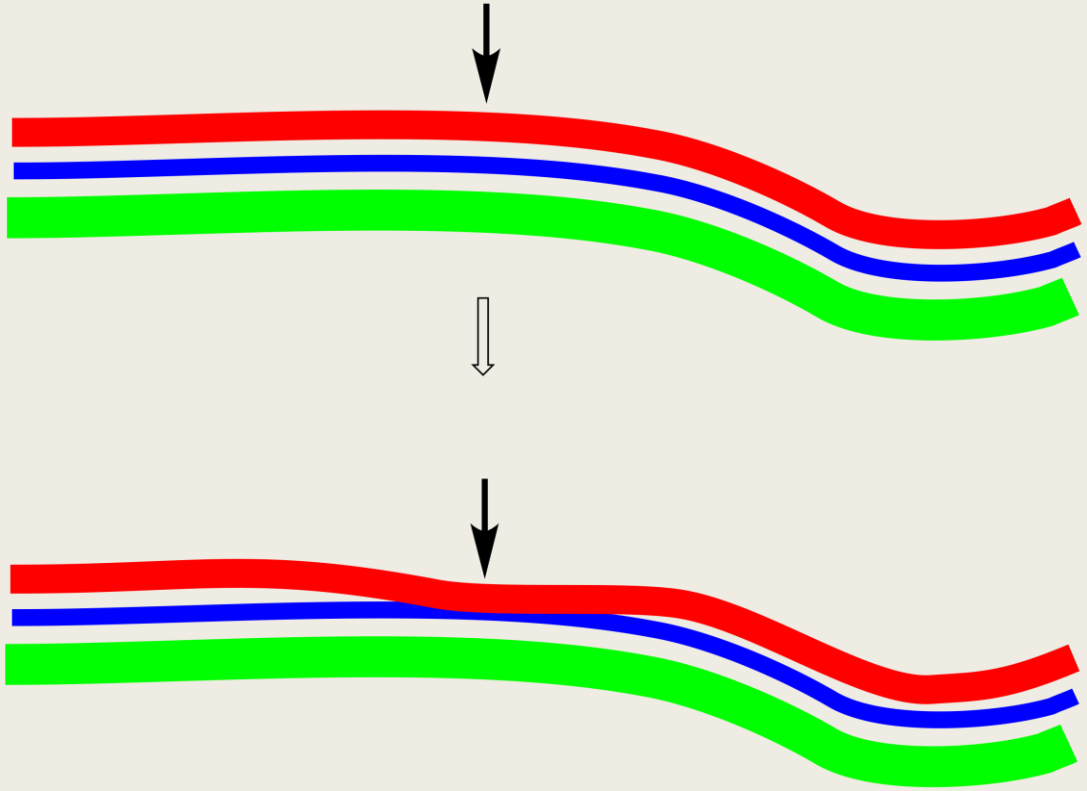
Above glass transition temperature

- Stress accommodated by local chain flow; bending; ***rubbery***.



Below glass transition temperature

- Insufficient volume for chain flow; unyielding; ***glassy***.



Tacticity

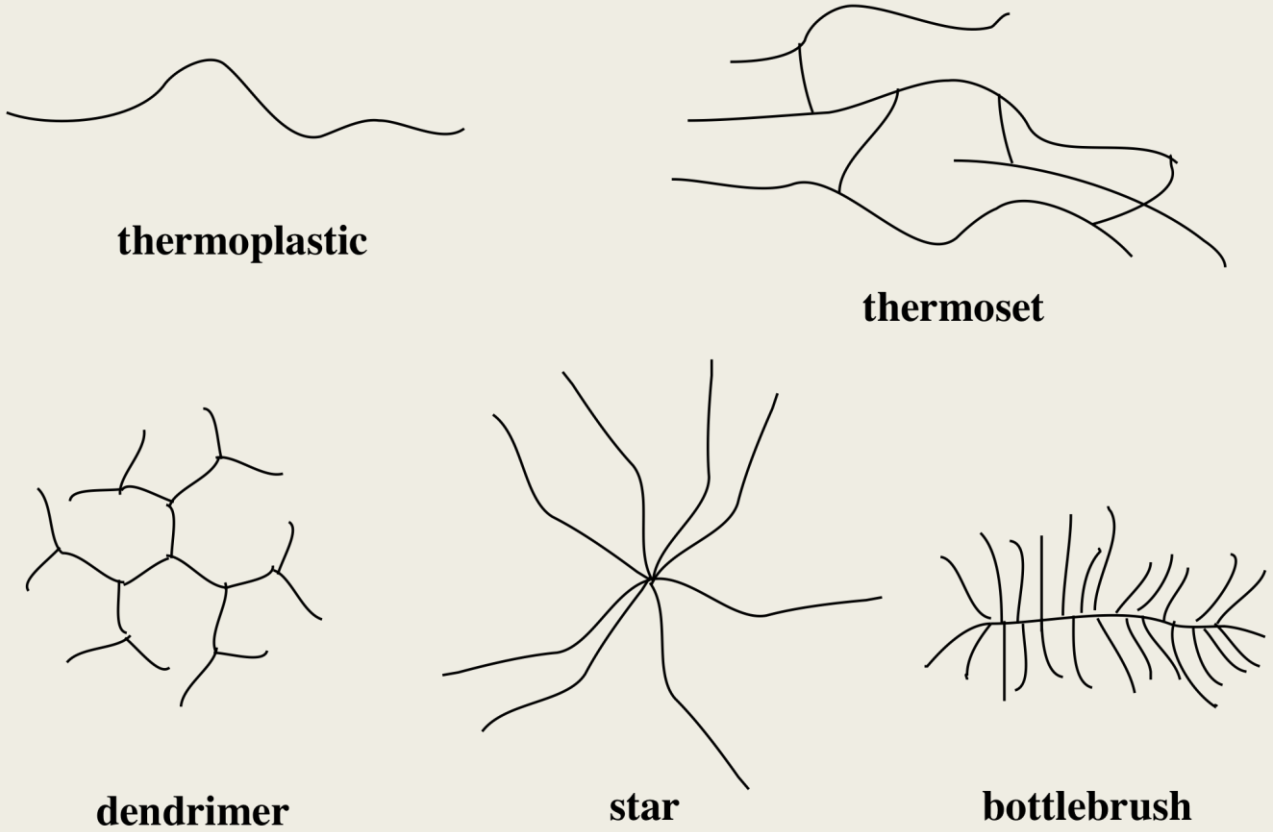
- Arrangements of groups in space around the backbone

isotactic polypropylene T_g = -18 ^oC

syndiotactic polypropylene T_g = -4 ^oC

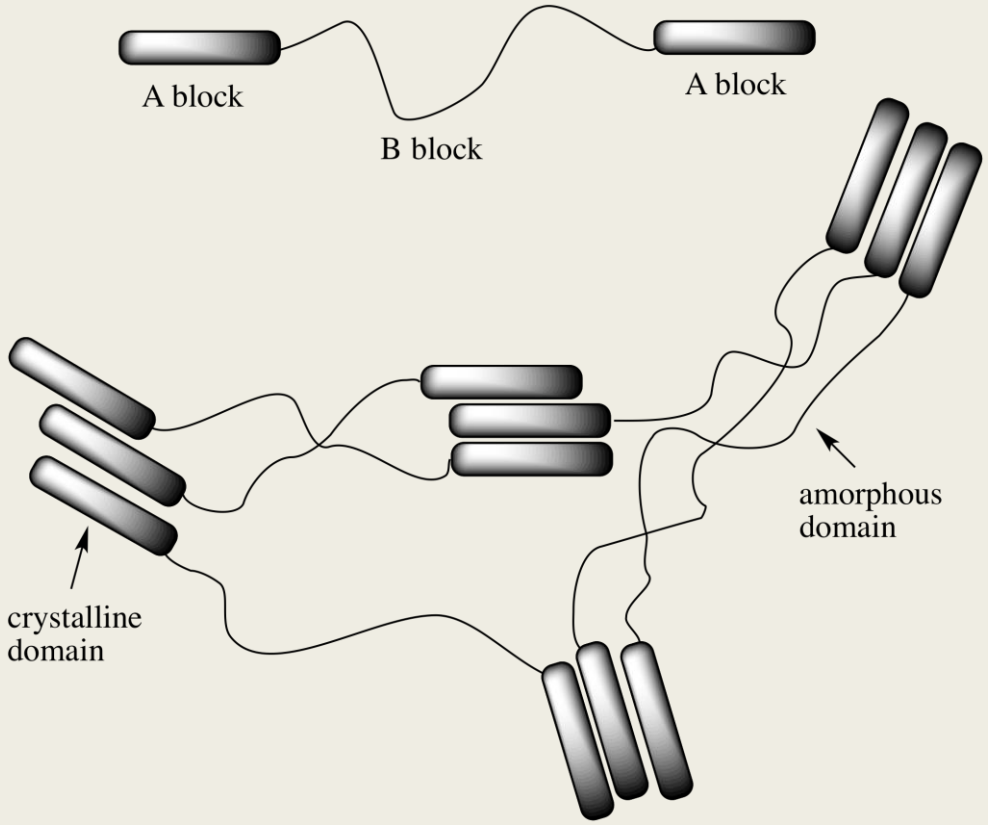
What makes polymers unique?

- Diverse architectures



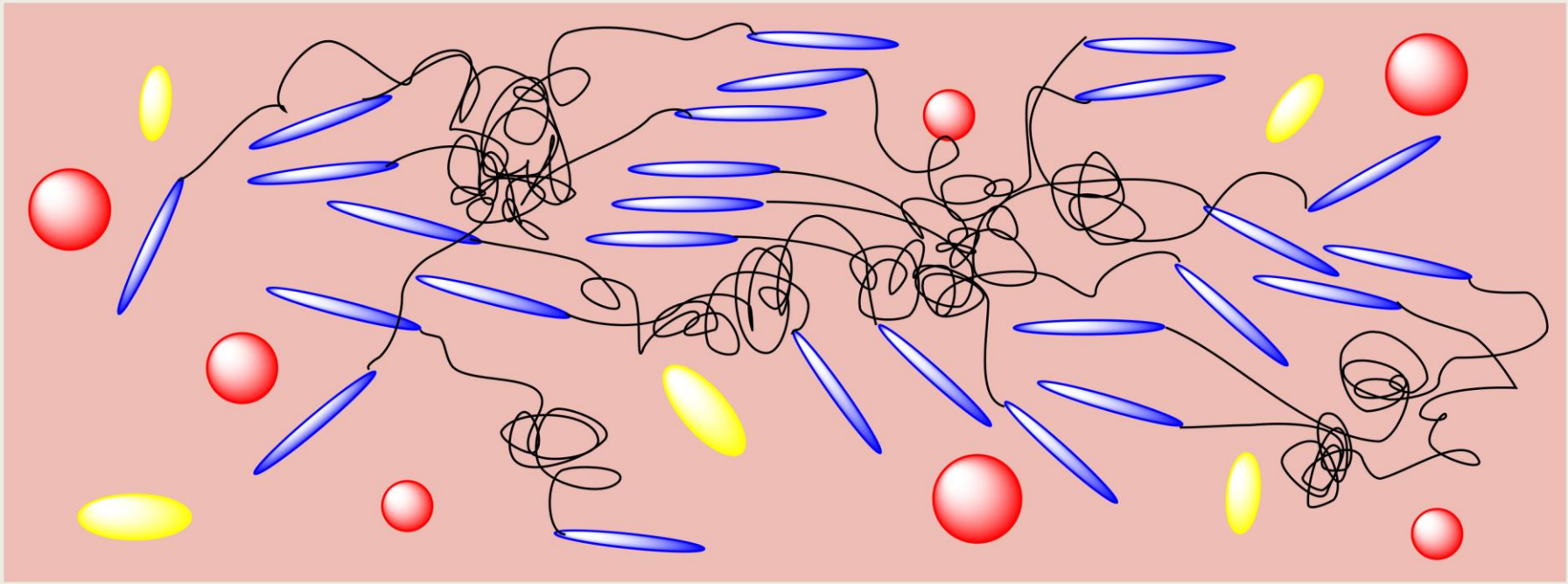
Co-polymers and microphase separation

- Amorphous and crystalline domains



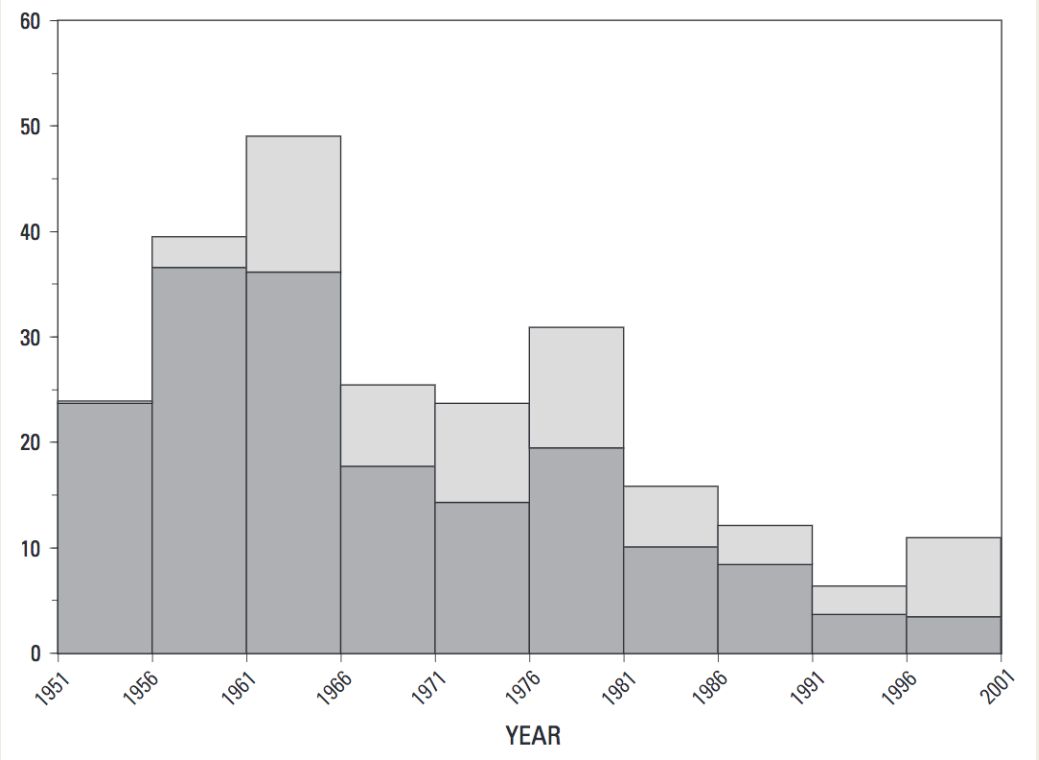
Chewing gum

- Microphase separation and viscoelastic response in block copolymers

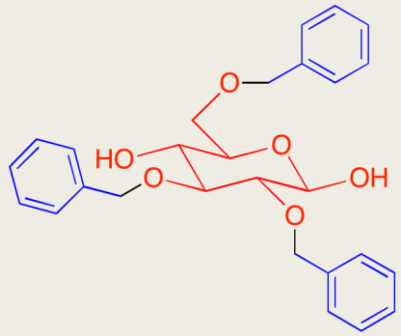


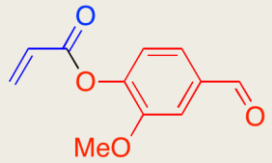
Why sustainable polymers?

- Petroleum discoveries by estimated recoverable volume per five year period:

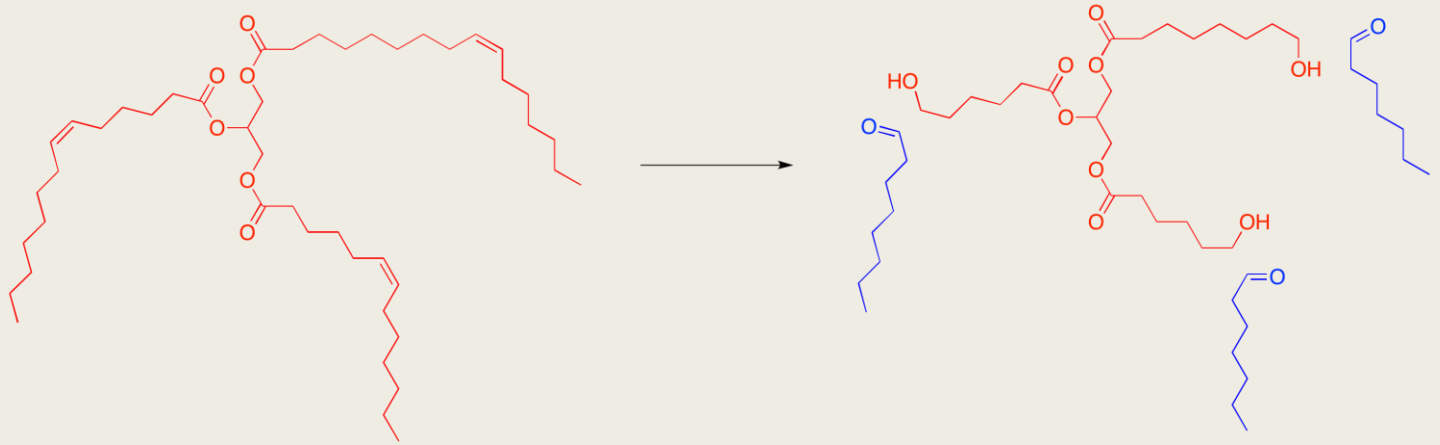


Sources of sustainable polymers

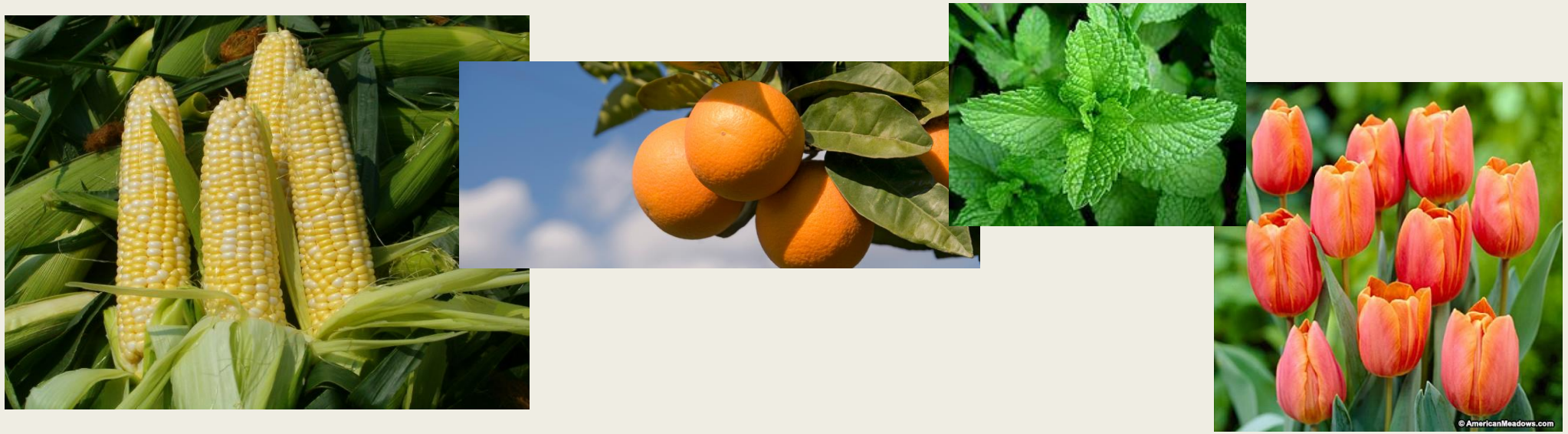


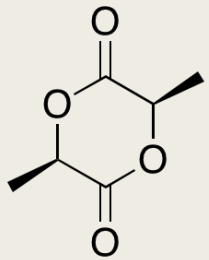


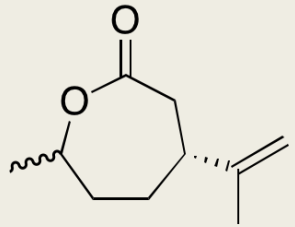
Sources of sustainable polymers

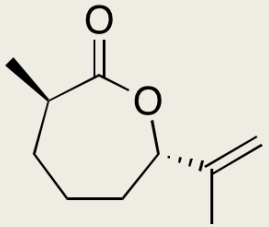


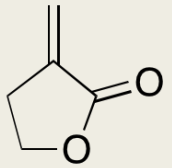
Sources of sustainable polymers









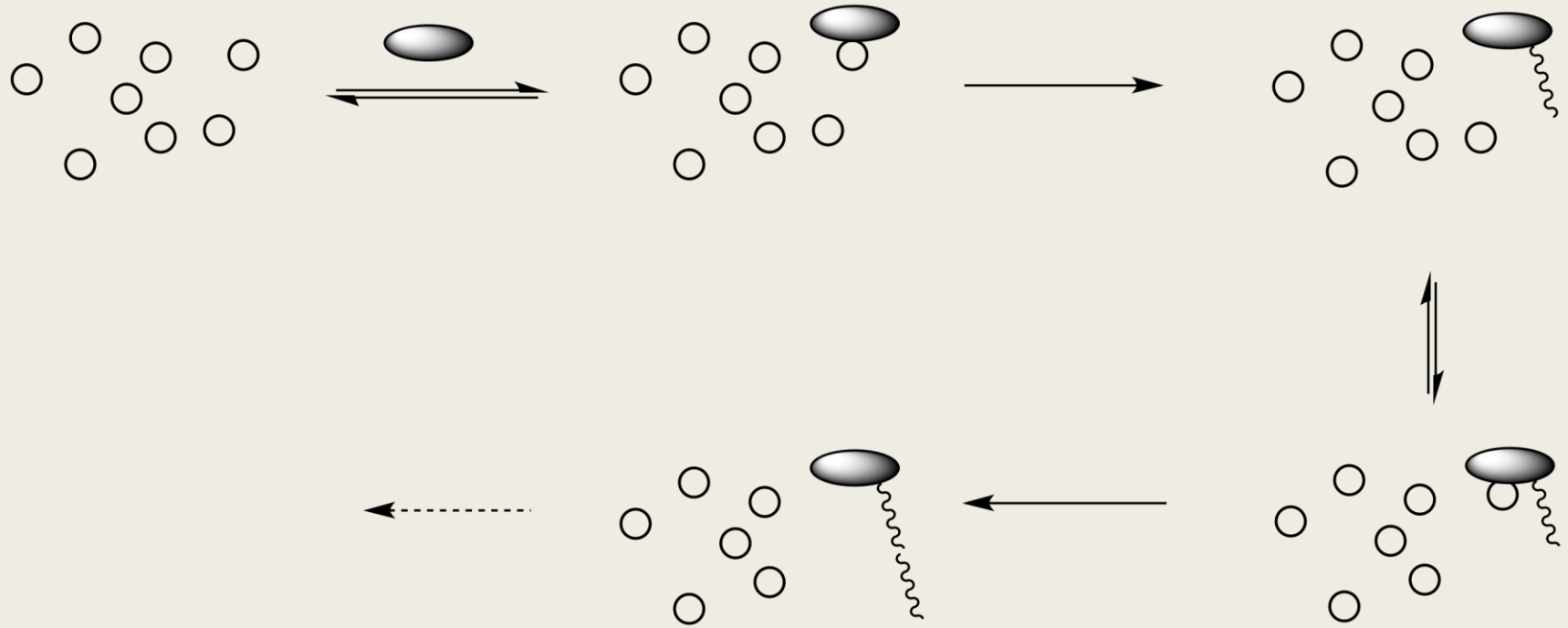


A commercially important example: PLA

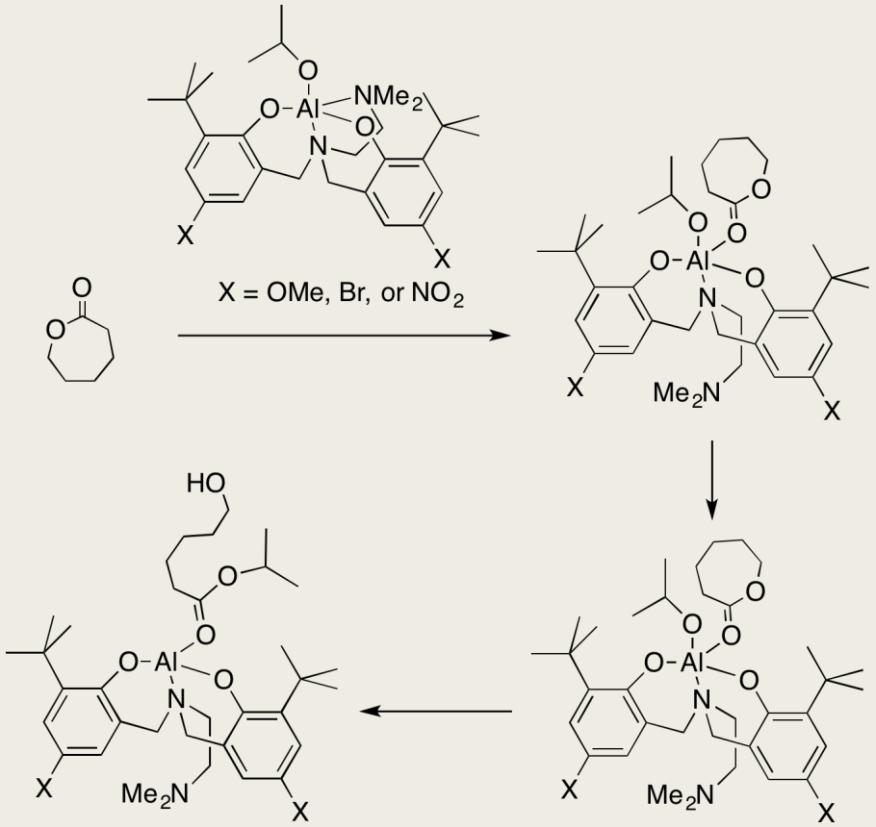
- From corn & soybeans
- Typically made from LA with FDA-approved tin catalyst
- Slightly hard, brittle
- Biodegradable with heat, moisture -- large-scale compost
- Food packaging
- Biomedical – time-lapse drug delivery

Understanding polymer formation

- 2-step: binding and opening



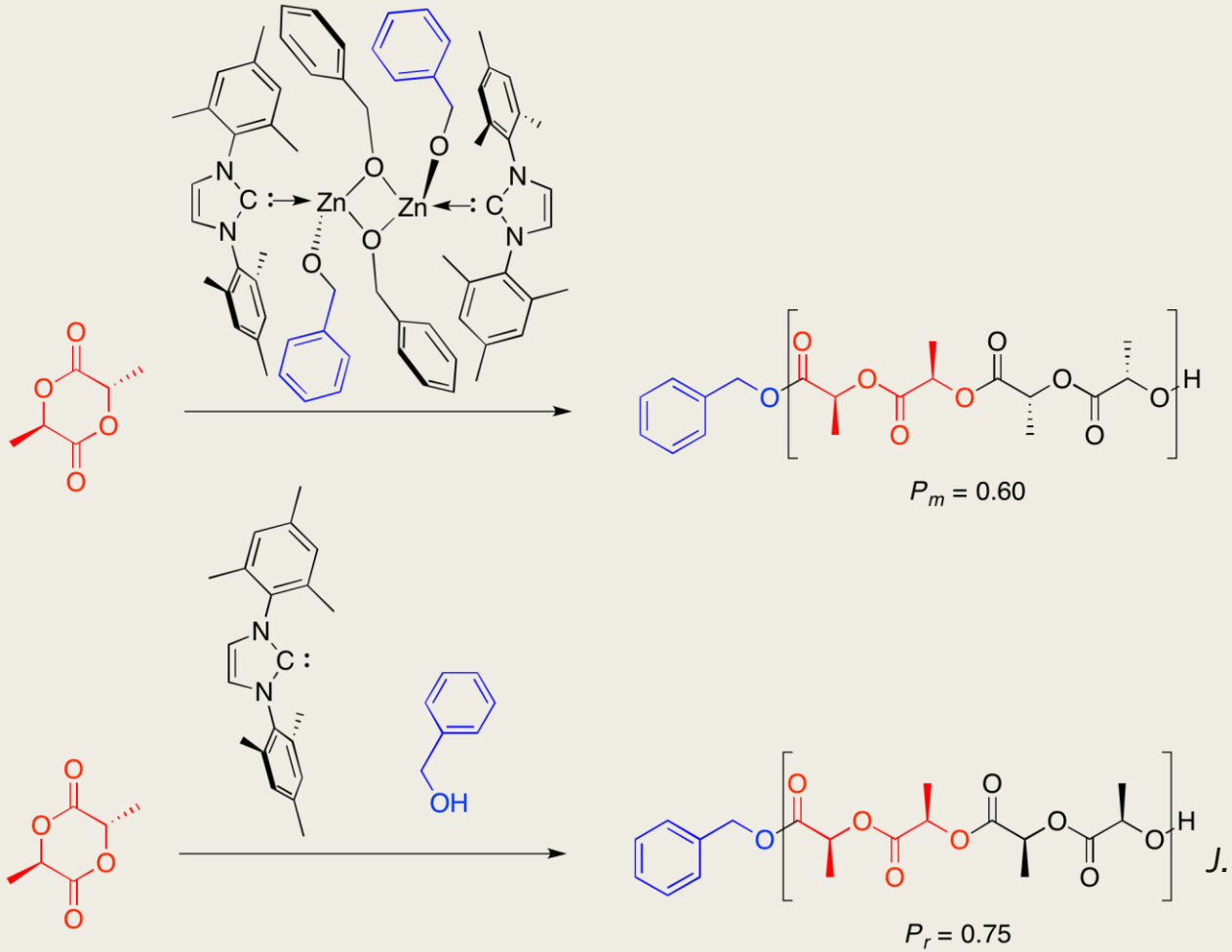
Mechanistic details



Stephanie Roe

- Macromolecules 2012, 45, 5387-5396.

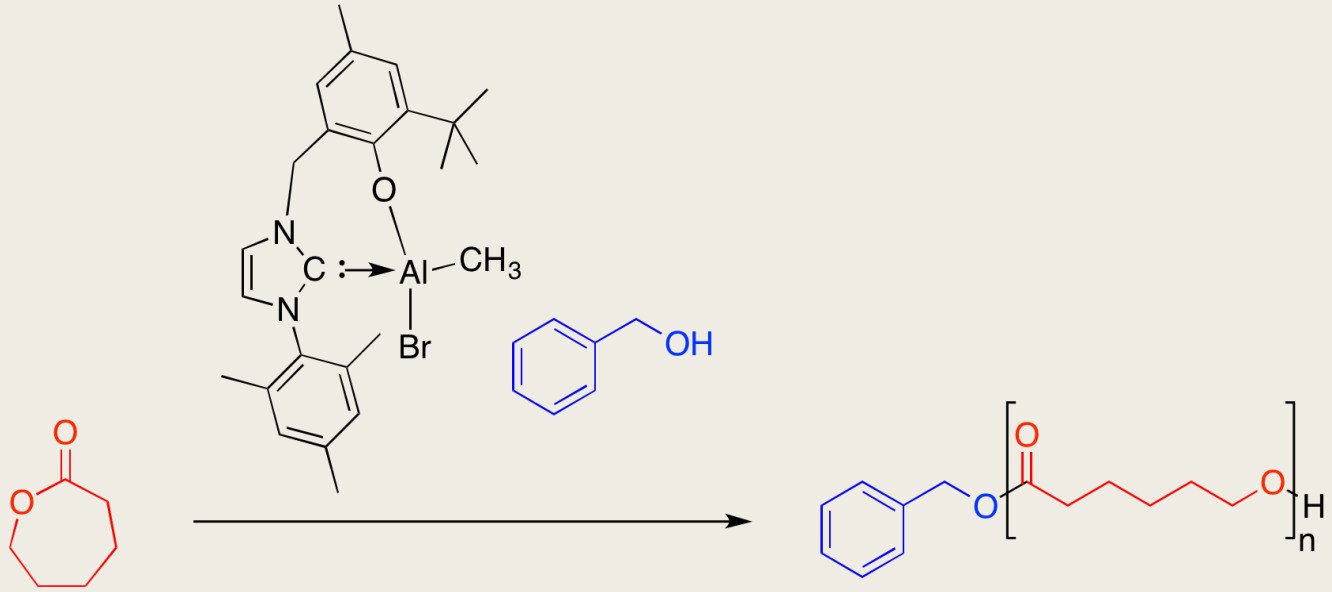
Building better catalysts



J. Organomet. Chem. **2005**, *690*, 5881-5891.

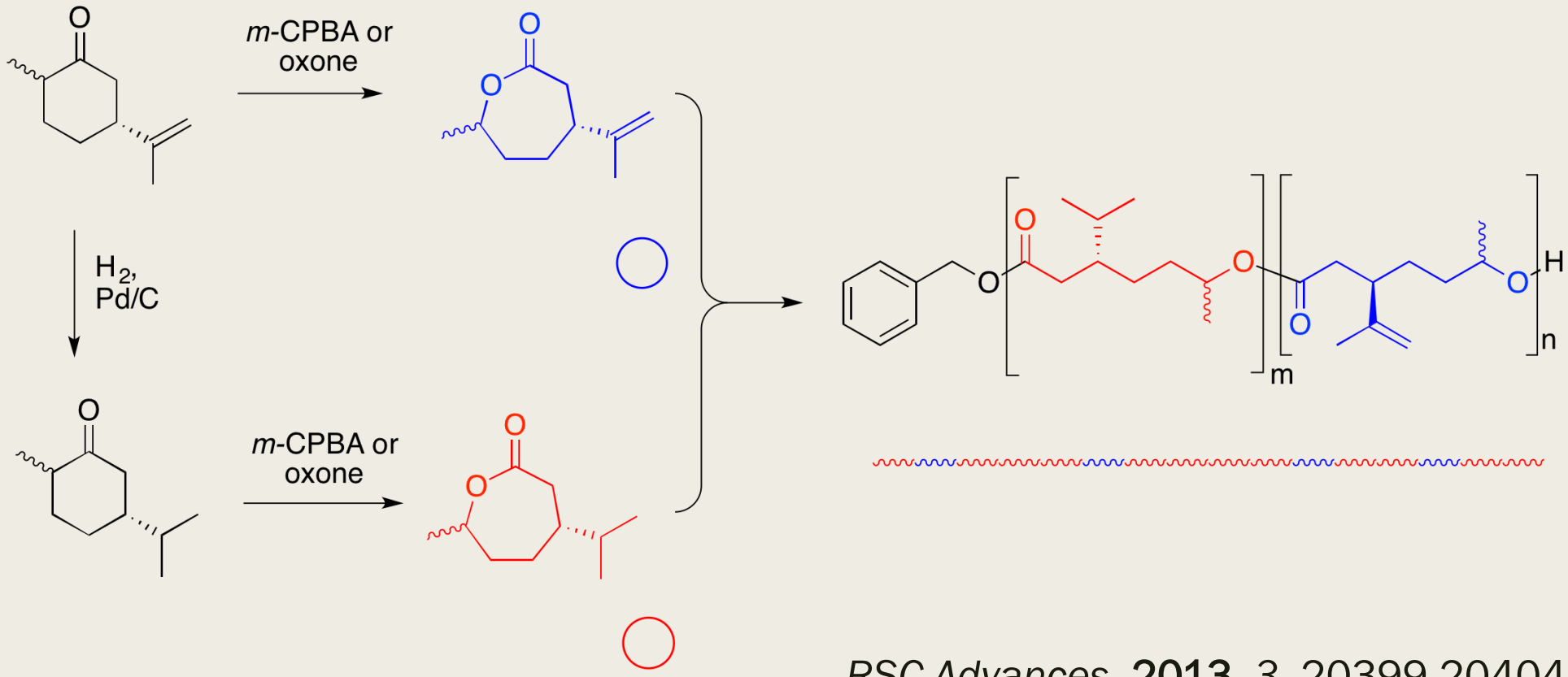
Building better catalysts

- Tie down the carbene ligand.



Davis Deanovic, Zoua Pa Vang, Stephanie Roe

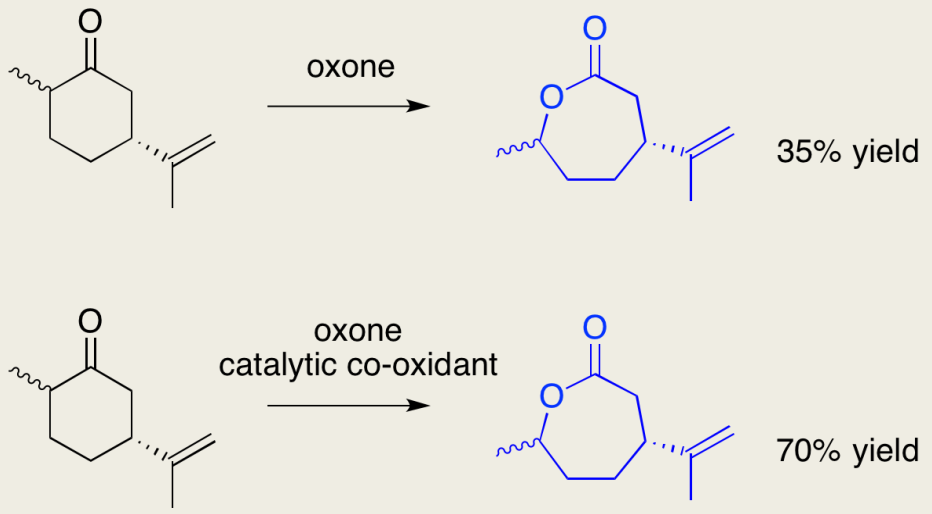
Making polymers: citrus-based chains



RSC Advances, **2013**, *3*, 20399-20404.

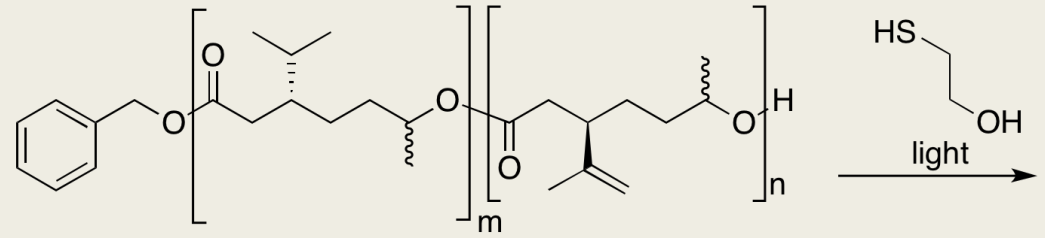
Making monomers

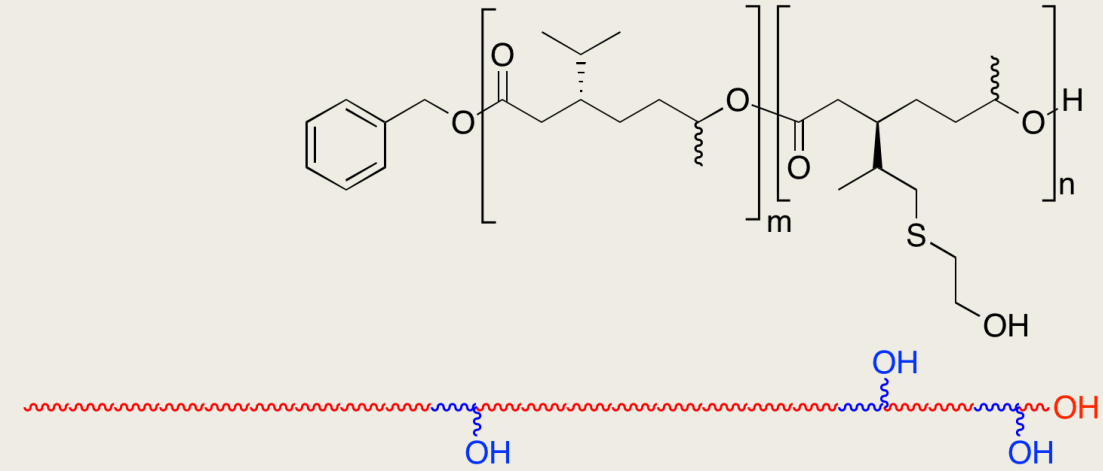
- Increased yield for increased sustainability.



Clare Johnston & Levi Salzl

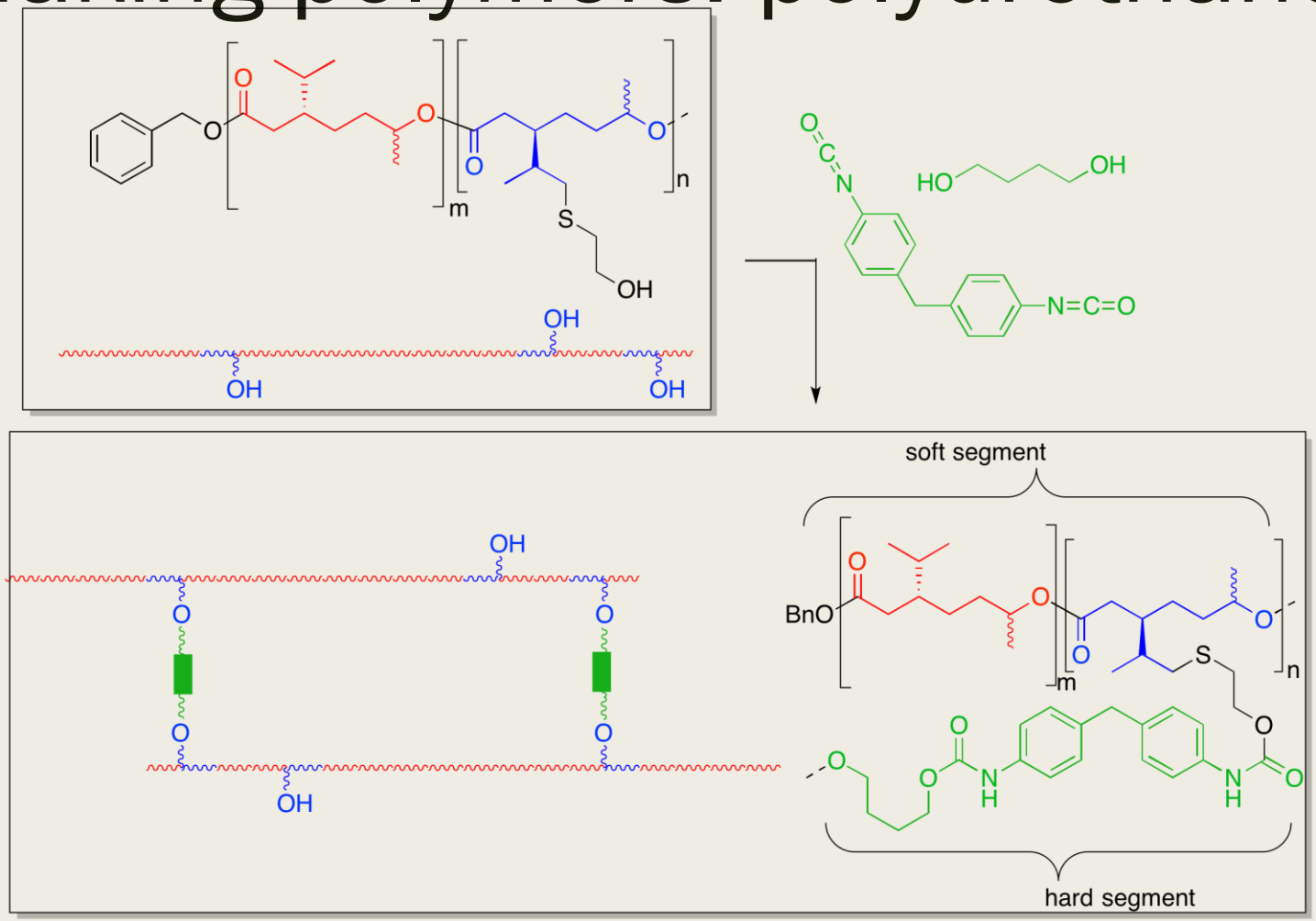
Making polymers: adaptation





RSC Advances, **2013**, *3*, 20399-20404.

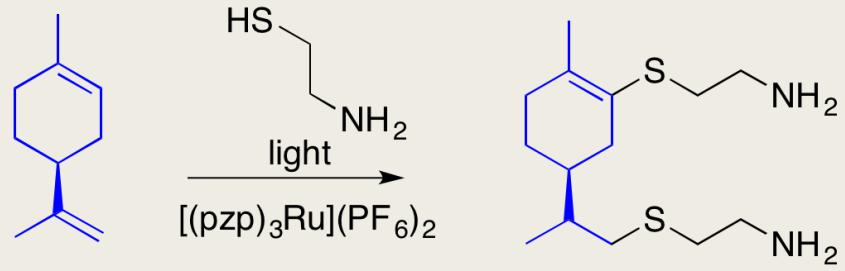
Making polymers: polyurethane



RSC Advances, **2013**, *3*, 20399-20404.

Ongoing adaptations

- Polymer (or monomers) with pendant amine groups.
- Polyureas, epoxy resins



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